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Large three-photon absorption and intramolecular charge transfer of the bis-donor fluorene-based molecules

Wenbo Ma[a,*], Yiqun Wu[a,b], Junhe Han[c], Donghong Gu[a], Fuxi Gan[a]

[a]*Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Shanghai 201800, People's Republic of China*
[b]*Laboratory of Functional Materials, Heilongjiang University, Haerbin 150080, People's Republic of China*
[c]*Department of physics, Henan University, Kaifeng 475001, People's Republic of China*

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Abstract

Three-photon absorption (3PA) of two fluorene-based molecules with D–π–D structural motifs (abbreviated as *BPAF* and *BCZF*) has been determined by using a Q-switched Nd: YAG laser pumped with 38 ps pulses at 1064 nm in DMF. The measured 3PA cross-sections are 222 and 140×10^{-78} cm^6 s^2 for *BPAF* and *BCZF*, respectively. AM1 calculations show that attaching different donors changes the charge density distribution of the fluorene skeleton, and it is observed that the 3PA cross-section can be enhanced with increasing intramolecular charge transfer character, measured by the parameter $\Delta\rho_1/\Delta\rho_2/\Delta\rho_1{}'$.

Keywords: Three-photon absorption; Fluorene-based molecule; Intramolecular charge transfer

1. Introduction

Organic molecules with large three-photon absorption (3PA) cross-section have been found to be useful for a variety of applications such as multiphoton fluorescence imaging [1–3], up-converted stimulated emission [4], optical limiting [5–7] and light-activated therapy [8]. Therefore, it is quite important to understand the relationship between the molecular structure and the three-photon absorption cross-section to provide a guideline for organic synthetic approach to a new development of the 3PA chromophores and for further applications. Much effort has been undertaken recently to develop organic molecules with large three-photon absorption cross-sections, for example, the measured 3PA cross-sections σ'_3 for some stilbazolium-like dyes have been reported to be as high as 10^{-76} cm^6 s^2 at 1064 nm for ps pulses by Wang et al [6,7]. Hernández [9] investigated the 3PA cross-sections of two fluorene derivatives with donor–bridge–donor (D–π–D) and donor–bridge–acceptor (D–π–A) structural motifs, it was shown that symmetric intramolecular charge transfer in the D–π–D molecule enhances 3PA in these fluorene derivatives. Furthermore, in our recently theoretical and experimental investigations [10], we found that a major contribution to the σ'_3 values originates from the transition dipole moment from the ground state to lowest charge transfer excited state. Also, increasing the conjugation length and increasing the charge-transfer dimensionality would be valuable to enhance the 3PA cross-sections.

In this letter, we investigate a class of fluorene derivatives with the same symmetric, D–π–D, conjugated structure, which are named as 9, 9-diethylhexyl-2, 7-bis-(*N*,*N*-diphenylamine) fluorene (*BPAF*) and 9, 9-diethylhexyl-2, 7-bis- (*N*, *N*-carbazole) fluorene (*BCZF*). In an effort to make clear the mechanism for enhancement of three-photon absorption cross-sections in D–π–D conjugated molecules, we use intensity dependent transmission measurement to obtain the three-photon absorption cross-sections of these two molecules at 1064 nm pumped with ps laser, and combined with the quantum chemistry calculations, the influence of intra-molecular charge transfer on three-photon absorption cross-sections are discussed micromechanically.

* Corresponding author. Tel.: +86 21 6991 8592; fax: +86 21 6991 8800.
E-mail address: ma_wenbo@mail.siom.ac.cn (W. Ma).

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2. Experiment

2.1. Materials

The chemical structures of the fluorene-based molecules under study are shown in the top-right corner in Fig. 1. In *BPAF* and *BCZF* the central fluorene is symmetrically end-capped with donor groups (*N*, *N*-diphenylamine and *N*-carbazole, respectively) forming a D–π–D sequence. These two molecules were all synthesized by Cu-mediated Ullmann condensations reactions [11], and the chemical structure of these two molecules has been identified by elemental analysis, MS, IR spectrum, and UV–Vis spectrum. The linear absorption spectrum and one-photon fluorescence spectrum were measured by using Lambda 9 UV/Vis/NIR recording spectrophotometer and FP-6500 fluorescence spectrometer, respectively. These two molecules solution in DMF with a concentration of 1.4×10^{-5} mol/l filled in a 1-cm-path quartz cuvette was used for both measurements.

2.2. Measurement of non-linear transmission

In the measurement of non-linear transmission, the incident 1064 nm lasing was provided by a Q-switched Nd: YAG laser (Continuum, PY61C-10) with pulse duration of 38 ps, repetition rate of 10 Hz. The laser beam was separated into two beams by the beam splitter (BS). The weaker beam, detected by a photodiode PD1, was used to monitor the incident laser energy. The stronger beam, being focused into the sample by a 25 cm focal-length lens, acted as the exciting beam. The entire transmitted intensities through the sample were totally collected to a photodiode PD2. These two photodiodes were connected with a two-channel energy meter (Molectron EPM 2000) to record the input and output energy simultaneously. The pump energy was controlled by rotating a half-wave plate between two polarizers. The input energy was adjusted from low to high and corresponding output energy can be obtained simultaneously.

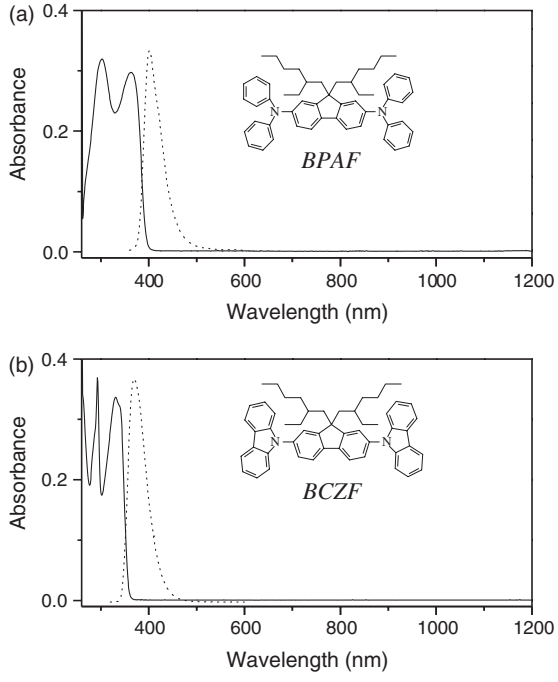


Fig. 1. Linear absorption (solid line) and one-photon fluorescence spectra (doted line) of *BPAF* and *BCZF* in DMF at a concentration of 1.4×10^{-5} mol/l.

2.3. Quantum chemistry calculations

Ab initio calculations were performed on an AMD XP 2500+(1.84 GHz) personal computer with 256 MB of RAM using $G_{AUSSIAN}$ 98 W program, version 5.1 [12]. The optimized geometries of two molecules and charge density distributions in both ground- and excited-state were calculated using AM1 semi-empirical method in the MOPAC quantum chemical package [13]. The excited states are characterized, and the electronic transitions are computed by ZINDO/S method [14,15] at the optimized geometries.

3. Results and discussions

3.1. Linear absorption and fluorescence emission

Fig. 1 shows the linear absorption and emission spectra of 9, 9-diethylhexyl-2, 7-bis- (*N*, *N*-diphenylamine) fluorene (*BPAF*) and 9, 9-diethylhexyl-2, 7-bis- (*N*, *N*-carbazole) fluorene (*BCZF*) in DMF solution. The both two molecules show strong UV absorption in the spectral range of 260–400 nm. In Fig. 1a, the two peaks identified at ca. 300 and 360 nm correspond to transitions $S_0\rightarrow S_2$ and $S_0\rightarrow S_1$, respectively [16]. In Fig. 1b, the same corresponding transitions are evident at approximately 295 and 330 nm. It also can be that there is no one-photon absorption for these two molecules in the entire near IR and most (>400 nm) of the visible spectral range. The three-photon energy of 1064 nm radiation just falls into the strong UV absorption, and therefore three-photon absorption in this solution may be expected. The one-photon fluorescence spectrums of two molecules are also shown in Fig. 1 by a dotted line. One can find that the fluorescence band of these two molecules is located at blue–violet region with the peak wavelength of 400 and 370 nm, respectively. Because of the high molecular symmetry, small Stoke's shift was observed, which can be explained by a small change in the molecular dipole moment upon electronic excitation [16].

3.2. Three-photon absorption cross-sections

Using intensity dependent transmission measurement we measured the three-photon absorption coefficients for both

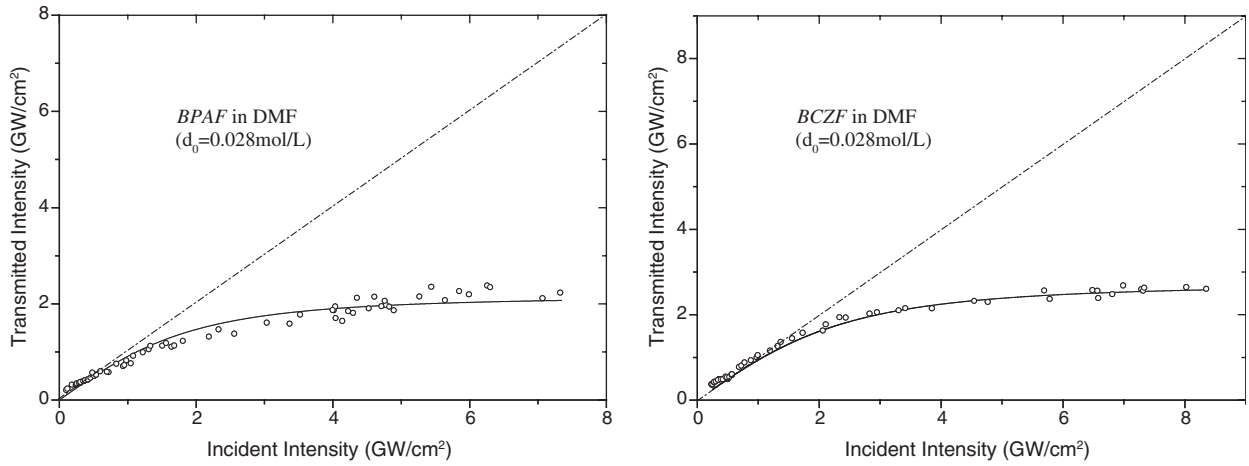


Fig. 2. Transmitted intensity as a function of the incident intensity for *BPAF* and *BCZF* of $d_0 = 0.028$ M/L (open circles). The solid curve are the theoretically fitted curve with a best-fit parameter of $\gamma_{BPAF} = 1.07 \times 10^{-19}$ cm^3/W^2 and $\gamma_{BCZF} = 6.78 \times 10^{-20}$ cm^3/W^2.The propagation distance of the excitation 1064 nm laser beam within the sample was 1 cm.

fluorene molecules in DMF solution with concentration of 0.028 mol/l at 1064 nm wavelength. In Fig. 2, the transmitted intensity as a function of the incident intensity is illustrated. The solid lines represent the theoretically fitted curve derived using basic theoretical considerations for three-photon absorption. Neglecting linear absorption at the pump wavelength, the intensity change of an excitation beam along the optical propagation path z is simply written as

$$dI(z)/dz = -\gamma I^3(z) \tag{1}$$

where γ is the three-photon absorption coefficient of the given sample medium. The solution of Eq. (1) can be simply obtained as [5]

$$I(z) = I_0/\sqrt{(1 + 2\gamma z I_0^2)} \tag{2}$$

where I_0 is the incident intensity of the excitation beam. From the relationship between $I(z)$ and I_0, the three-photon absorption coefficient γ can be easily deduced.

The γ values corresponding to the best fit are 1.07×10^{-19} and 6.78×10^{-20} cm^3/W^2, respectively. Based on the known γ value of the measured solution sample, the molecular absorption cross-section σ'_3 (in the units of cm^6 s^2) for given sample in solution is obtained by [9]

$$\sigma'_3 = \frac{\gamma}{N_A \times d_0 \times 10^{-3}} \left(\frac{hc}{\lambda}\right)^2 \tag{3}$$

here, N_A is Avogadro constant, d_0 is the concentration of the sample in solution (in the units of mol/l), and $h(c/\lambda)$ is the energy of an incident photon at 1064 nm. So the intrinsic sample molecular σ'_3 values can be easily estimated as 222 and 140×10^{-78} cm^6 s^2 for *BPAF* and *BCZF*, respectively. Due to the influence of the quartz and the uncertainty of the incident intensity, the final results of γ and σ'_3 of these two molecules have an experimental uncertainty of 10%. It can be easily found that the measured values of σ'_3 for the two compounds are as high as 10^{-76} cm^6 s^2 for ps pulses. These values are comparable to that of 2,5-bisbenzothiazole-3, 4-didecyloxy thiophene (BBTDOT) [5] and 6-propionyl-2-dimethyl-amino-naphthalene (PRODAN) [17] at 1064 nm for ns pulses, and in the same order of magnitude for previously reported stilbazolium and stilbazolium-like derivatives under the similar experiment conditions [6,7]. Additionally, by comparison of the σ'_3 values of *BPAF* and *BCZF* measured in picoseconds at 1064 nm, we have found that the σ'_3 value for *BPAF* is almost 1.6 times greater than that for *BCZF*. We consider that such large differences must originate from fundamental variations in the chemical structures of these two molecules. Using AM1 semi-empirical method, we calculated the charge density distributions in both ground- and excited-state of these two molecules and found that substantial charge density redistributions upon excitation are related to 3PA cross-sections.

3.3. Electronic excitations and intramolecular charge transfer

Recently, theoretical investigation revealed that there are more possible transition paths from ground to final states, S_f, involved in a three-photon absorption process, such as (I) $S_0 \rightarrow S_i \rightarrow S_j \rightarrow S_f$, (II) $S_0 \rightarrow S_f \rightarrow S_0 \rightarrow S_f$, (III) $S_0 \rightarrow S_i \rightarrow S_i \rightarrow S_f$, (IV) $S_0 \rightarrow S_i \rightarrow S_f \rightarrow S_f$, (V) $S_0 \rightarrow S_f \rightarrow S_f \rightarrow S_f$. Among them, path (II) is present in both symmetrical and asymmetrical systems and is also an important contributor. In other words, a strong one-photon absorption state can be a strong 3PA state as well [18]. The ZINDO/S semi-empirical method has been used to obtain the nature and the energy of the first 10 singlet-singlet electronic transitions of *BPAF* and *BCZF* at the AM1 optimized geometry and we find that the first excited state, S_1, is the strongest one-photon absorption state for these two fluorene-based molecules. Excitation to the S_1 state corresponds almost

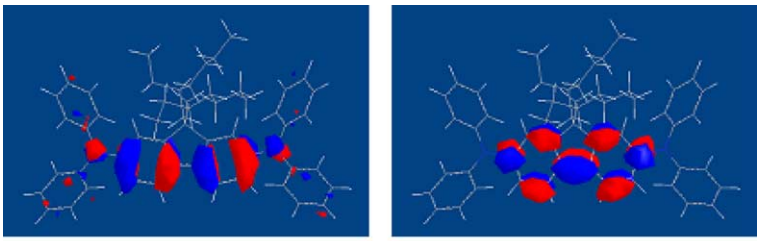


Fig. 3. Charge density distributions of *BPAF* in (a) HOMO and (b) LUMO

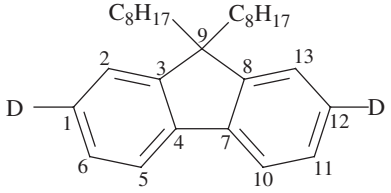
exclusively to the promotion of an electron from the HOMO to the LUMO, which are both delocalized over the whole molecule (Take *BPAF* for example, the result is shown in Fig. 3). From Fig. 3, it can be easily found that the substantial symmetric charge redistribution occurs upon excitation.

The charge density distributions of *BPAF* and *BCZF* in both ground- and excited-state were calculated using AM1 semi-empirical method. Correspondingly, the molecular structure changes from KéKule-type in the ground-state to the quinine-type in the excited-state [19–21], accompanied with the intra-molecular charge transfer. The related data are presented in Table 1. Charge density redistribution can reflect the extent of resonance interaction between two donors, which in turn indicates the extent of intra-molecular charge transfer. We divide the molecular structure into three parts: ρ_1, ρ'_1, and ρ_2. Here, ρ_1 and ρ'_1 describe the average charge densities on the donor (D), and the donor ability is indicated here by the π-electron density on the N atom, while ρ_2 describes the corresponding average value for atoms C1 to C13 on the π-framework (excluding C9). The charge densities difference between the first excited state (S_1) and ground state (S_0), $\Delta\rho_1/\Delta\rho_2/\Delta\rho'_1$, is thus an intra-molecular charge transfer character. The unit of charge on every atom is *e*. From Table 1, one can see that $\Delta\rho_2$ in the naked skeleton is negligible (0.0070*e*), but once the skeleton has been attached donor–donor pair, then $\Delta\rho_2$ becomes significant, and this change will influence three-photon absorption cross-section. It is interesting to note that large intra-molecular charge transfer, $\Delta\rho_1/\Delta\rho_2/\Delta\rho'_1$, contribute to enhancing 3PA cross-section. Obviously, *BCZF* has small σ'_3 value (140×10^{-78} cm^6 s^2) because it possesses small $\Delta\rho_1/\Delta\rho_2/\Delta\rho'_1$ ($+0.1604/+0.4035/+0.1600e$), on the other hand, *BPAF* exhibit larger σ'_3 value (222×10^{-78} cm^6 s^2) since it possesses larger $\Delta\rho_1/\Delta\rho_2/\Delta\rho'_1$ ($+0.2046/+0.4680/+0.2062e$), which indicated that the degree of symmetric intramolecular charge transfer occurred in *BPAF* is larger than *BCZF*. Therefore, the charge redistribution in the bis-donor conjugated molecules is more important for enhancing 3PA cross-section.

4. Conclusions

In summary, two novel symmetrical charge transfer fluorene-based molecules, *BPAF* and *BCZF*, have been synthesized. The 3PA effect of these two molecules was demonstrated at 1064 nm and the measured 3PA cross-section of *BPAF* and *BCZF* are as high as 10^{-76} cm^6 s^2. Charge density redistribution (defined by $\Delta\rho_1/\Delta\rho_2/\Delta\rho'_1$) in the molecular skeleton was calculated by the AM1 semi-empirical method. The experimental and theoretical results demonstrated that the charge density redistribution ($\Delta\rho_1/\Delta\rho_2/\Delta\rho'_1$) has a significant effect on the 3PA cross-section, which increases with an increase in the $\Delta\rho_1/\Delta\rho_2/\Delta\rho'_1$ value.

Table 1
Three-photon absorption cross-sections (σ'_3) and the charge density distributions of ground-and excited-state ($\rho_1/\rho_2/\rho'_1$)



Molecules	3PA cross-sections σ'_3 ($\times10^{-78}$ cm^{6}s^2)	$\rho_1/\rho_2/\rho'_1$ (*e*)	$\Delta\rho_1/\Delta\rho_2/\Delta\rho'_1$ (*e*)
Naked skeleton	–	–/−1.6983/– (S_0) –/−1.6913/– (S_1)	–/+0.0070/–
BPAF	222	−0.3162/−1.1829/−0.3169 (S_0) −0.1116/−0.7149/−0.1107 (S_1)	+0.2046/+0.4680/+0.2062
BCZF	140	−0.2644/−1.1209/−0.2658 (S_0) −0.1040/−0.7174/−0.1061 (S_1)	+0.1604/+0.4035/+0.1600

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References

[1] M. Gu, Opt. Lett. 21 (1996) 988.
[2] S. Maiti, J.B. Shear, R.M. Williams, W.R. Zipfel, W.W. Webb, Science 275 (1997) 530.
[3] R. Naskrecki, M. Menard, P. VanderMeulen, G. Vigneron, S. Pommeret, Opt. Commun. 153 (1998) 32.
[4] G.S. He, P.P. Markowicz, T.-C. Lin, P.N. Prasad, Nature 415 (2002) 767.
[5] G.S. He, J.D. Bhawalkar, P.N. Prasad, Opt. Lett. 20 (1995) 1524.
[6] C. Zhan, D. Li, D. Zhan, Y. Li, D. Wang, T.X. Wang, Z.Z. Lu, L.Z. Zhao, Y.X. Nie, D.B. Zhu, Chem. Phys. Lett. 353 (2002) 138.
[7] D. Wang, C. Zhan, Y. Chen, Y.J. Li, Z.Z. Lu, Y.X. Nie, Chem. Phys. Lett. 369 (2003) 621.
[8] P.N. Prasad, Molecular Crystals and Liquid Crystals 415 (2004) 1.
[9] F.E. Hernández, K.D. Belfield, I. Cohanoschi, Chem. Phys. Lett. 391 (2004) 22.
[10] W. Ma, Y. Wu, J. Han, D. Gu, F. Gan, Chem. Phys. Lett. 403 (2005) 405.
[11] K.D. Belfield, K.J. Schafer, W. Mourad, B.A. Reinhardt, J. Org. Chem. 65 (2000) 4475.
[12] M.J. Frisch, GAUSSIAN 98W, Gaussian Inc., Pittsburgh, PA, (1998).
[13] J.J.P.J. Srewar, Comput. Chem. 209 (1989) 221.
[14] J. Ridley, M.C. Zerner, Theor. Chim. Acta. 32 (1973) 111.
[15] C. Forber, M.C. Zerner, J. Am. Chem. Soc. 107 (1985) 5884.
[16] K.D. Belfield, M.V. Bondar, O.V. Przhonska, K.J. Schafer, W. Mourad, J. Fluorescence. 97 (2002) 141.
[17] J.D. Bhawalkar, G.S. He, P.N. Prasad, Opt. Commun. 119 (1995) 587.
[18] P. Cronstrand, Y. Luo, P. Norman, H. Ågren, Chem. Phys. Lett. 375 (2003) 233.
[19] I.D.L. Albert, T.J. Marks, M.A. Ratner, J. Am. Chem. Soc. 119 (1997) 6575.
[20] F. Meyers, S.R. Marder, B.M. Pierce, J.L. Brédas, J. Am. Chem. Soc. 116 (1994) 10703.
[21] T. Kogej, D. Beljonne, F. Meyers, J.W. Perry, S.R. Marder, J.L. Brédas, Chem. Phys. Lett. 298 (1998) 1.